species prevents the existence of metal-metal bonds in the ground-state geometry. However, the symmetric bending motion of the M-C-M framework should allow the two metal atoms to form a three-membered transition state for the elimination of a CO molecule. Localization of a sufficient number of vibrational quanta in this bending mode is more likely for the copper species. The greater center-of-mass energy available for collisional activation of the copper species explains the greater abundance of the Cu_2CO^+ ion in the Cu_2^+ ion parent ion MS/MS spectrum compared to the Ag_2CO^+ ion in the Ag_2^+ ion parent ion MS/MS spectrum.

The M_2O^+ ions are predicted to have linear M-O-M ground-state structures, which precludes the existence of a metal-metal bond. The presence of this ion in the metal dimer ion parent ion MS/MS spectra is explained by rearrangement of a small fraction of the ground-state ion population to an excited-state M-M-O geometry. This excited-state geometry requires only simple cleavage of the M-O bond to form the metal dimer ion.

The present computational method also provides useful information about electronic structures of transition-metal-containing ionic species. With the exception of the Cu_2CO^+ ion, the copper species examined in this study are bound primarily by three-center, two-electron bonds. Since they contain an odd number of electrons, the metal atoms in the Cu_2CO^+ ion are bound to the CO molecule by the equivalent of a three-center, one-electron bond. The 3d atomic orbitals are not as involved because they are much less diffuse than the 4s atomic orbitals and are buried inside the 4s atomic orbitals. In contrast, the bonding in the silver-containing species studied cannot be described in this way. The same three-center, two-electron and three-center, one-electron bonds exist in the silver-containing species. However, the 4d atomic orbitals are more involved in the bonding. The 4d atomic orbitals of silver are much more diffuse than the 3d atomic orbitals of copper because of the larger number of core electrons in a silver atom. The core electrons more effectively shield the 4d electrons from the nucleus, thus making them more diffuse.

The predictive results of this work suggest that the interpretation of MS/MS data is not always straightforward. The simple presence or absence of an ion formed in a specific fragmentation pathway may lead to erroneous structural assumptions in situations in which excited-state geometries can be accessed. For instance, Busch et al.[4] deduced that the $Ag_2CH_3^+$ ion incorporates a metal-metal bond; the present computational results suggest that this is *not* the case. Sufficient energy is available in the collisional activation to form alternate higher energy ion structures.

Overall, this work shows that the ECP method can predict ionic geometries and excited-state geometries that are consistent with MS/MS data and that aid in its interpretation. With more sophisticated methods of incorporating relativistic effects on bonding into the calculational methods for compounds containing heavy elements, as described by Ziegler et al.,[38] increased use of these methods for structure investigations can be foreseen.

Acknowledgment. We thank R. G. Cooks at Purdue University for the use of the triple-quadrupole mass spectrometer. This work is part of the Ph.D. Thesis of R.A.F. at Indiana University.

Registry No. Ag_2H^+, 81900-29-0; Ag_2O^+, 133071-33-7; Ag_2CO^+, 133071-34-8; $Ag_2CH_3^+$, 106471-89-0; Ag_2, 12187-06-3; AgH, 13967-01-6; AgO, 1301-96-8; Cu_2H^+, 81900-28-9; Cu_2O^+, 116873-91-7; Cu_2CO^+, 133071-35-9; $Cu_2CH_3^+$, 133071-36-0; Cu_2, 12190-70-4; CuH, 13517-00-5.

Supplementary Material Available: Tables 2-13 giving population analyses and major components of molecular orbitals for Ag_2H^+, Cu_2H^+, $Ag_2CH_3^+$, $Cu_2CH_3^+$, Ag_2CO^+, and Cu_2CO^+ (20 pages). Ordering information is given on any current masthead page.

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ESCA Studies of Phase-Transfer Catalysts in Solution: Ion Pairing and Surface Activity

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Abstract: Phase-transfer catalysts in solution have been studied by means of electron spectroscopy. Different anion-cation distributions at the surface were found depending on the anion identity. Thus, tetrabutylammonium perchlorate and tributyl-3-iodopropylammonium iodide show strong evidence of the formation of contact ion pairs at the surface. Conversely, the tetrabutylammonium nitrate and chloride show a more diffuse character of the anion distribution with respect to the surface. The observed differences in surface structure between the salts correlate with the variation in transfer coefficients from aqueous to organic phase.

Introduction

Phase-transfer catalysis with tetraalkylammonium salts is an extremely powerful method in organic synthesis and has been employed in a multitude of applications since the pioneering work of Makosza,[1,2] Starks,[3] and Brändström.[4] The tetrabutylammonium ion is one of the most efficient catalytic agents in this group and has been the subject of several investigations using various methods, such as conductometric,[5-10] Raman,[11] IR,[12] and NMR[13] techniques. Measurements of electrolyte molar volume,[14]

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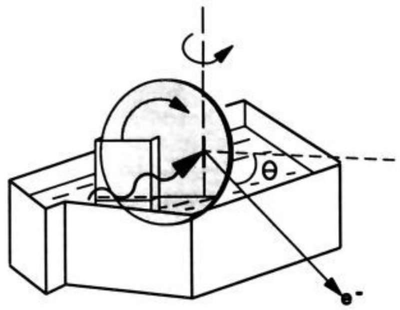

Figure 1. Schematic picture of the arrangement used for recording angular resolved electron spectra from solutions.

vapor pressure,[15] surface tension,[16] mobility,[17] and viscosity[10] provide additional information on the properties of solutions of the tetrabutylammonium salts.

We have previously reported on the use of ESCA (electron spectroscopy for chemical analysis) for the study of surfaces of solutions of tetraalkylammonium salts.[18,19] The main objective of those studies was the measurement of the cation distribution profile as obtained from photoelectron intensities recorded at different take-off angles with respect to the surface plane of the solution. In this angular resolved mode the technique allows variation of the bulk to surface contribution in the spectra within a distance from the surface equal to the mean free path of the photoelectrons ($\sim$25 Å). Whereas these previous investigations concentrated on the depth distributions of different tetraalkylammonium cations, the present study is aimed at the counteranion relation to the charged cation overlayer. Thus, comparative quantitative analysis of the surface concentrations of a number of anions is performed by using electron spectroscopy in the angular resolved mode for solutions containing the tetrabutylammonium ion as common cation (in one case substituted with iodine for a terminal methyl group). Our purpose is thus to study the specific chemical interactions involved in the ion pairing at the surface and possibly further elucidate the importance of these factors for the surface activity and phase-transfer efficiency. As in our previous investigations, we have used formamide as solvent. We believe that the properties of this solvent are sufficiently aqueouslike (e.g. concerning surface tension, dielectric constant, and solvent properties for both anions and cations) to render our results qualitatively valid also for water solutions. Formamide's advantage for ESCA lies in its low vapor pressure at room temperature.

Experimental Section

We have in a separate paper described in more detail the sample arrangement used to perform the measurements in the present paper.[20]

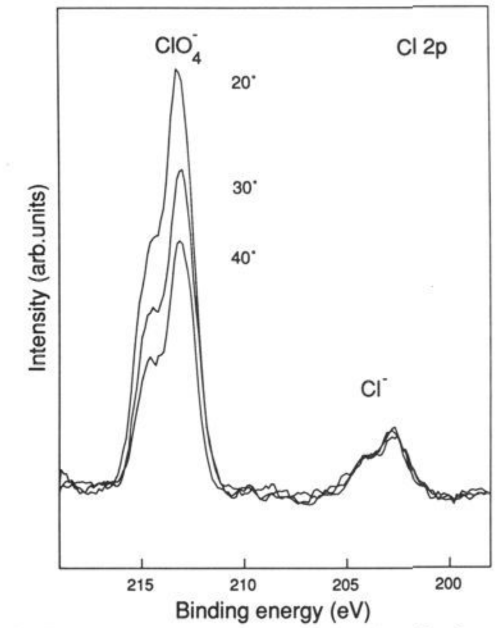

Figure 2. Cl 2p spectra recorded from a solution of tetrabutylammonium perchlorate (0.5 m) and potassium chloride (0.5 m) in formamide at three different photoelectron take-off angles (normalization with respect to the chloride peak).

The basic design is shown schematically in Figure 1. The essential feature is, as in our previous designs,[21,22] the use of a moving metal surface (in this setup in the form of a stainless steel disc) which acts as a backing for the sample. The disc is immersed in the liquid sample container whose form is adapted to the inside of the differentially pumped sample housing. The amount of liquid sample required is about 5 mL. The disc is rotatable around two different axes. One rotation continuously covers the metal substrate with fresh sample from the container. The other rotation is performed around the cross section line between the focus of the Al Kα X-ray monochromator and the acceptance to the electron spectrometer. In this way, the take-off angle of the electrons with respect to the sample surface plane can be varied continuously between 0 and 50°. This feature is essential for the surface applications reported here and allows detailed studies to be made of e.g. surface segregation profiles in liquid solutions. In our previous studies of such properties[18,19] only discrete angles could be measured in separate experiments. The present design allows the measurement of an extended angular interval to be made in one experiment, which implies a substantial gain in information rate over our old arrangement.

All spectra presented were obtained at room temperature and recorded from freshly prepared solutions. The spectra presented are typical recordings. Chemicals were commercial quality (purity > 98%) except for (IPrNBu$_3$)$^+$I$^-$, tributyl-3-iodopropylammonium iodide, which was prepared by us according to standard procedures.[23] Spectra are calibrated with respect to the vacuum level with use of the solvent C 1s line as reference.[24]

Results and Discussion

Figure 2 shows spectra recorded from a solution of tetrabutylammonium perchlorate mixed with potassium chloride in formamide. The concentration of the these two solutes was the same (0.5 m). The high binding energy Cl 2p peak (due to the perchlorate ion) is nevertheless seen to be of substantially higher intensity (by about a factor of 4 at 40°) than that of lower binding energy (due to the chloride ion). This clearly indicates formation of a surface active complex involving tetrabutylammonium and perchlorate ions. This complex is formed while the chloride ions

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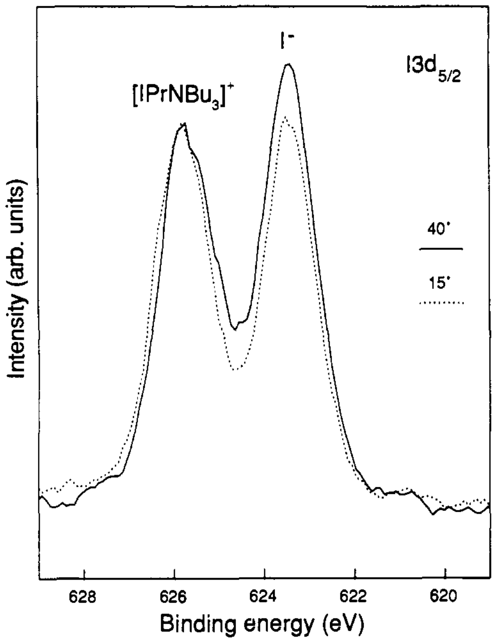

Figure 3. I $3d_{5/2}$ spectra obtained from a 0.5 *m* solution of $(IPrNBu_3)^+I^-$ in formamide at photoelectron take-off angles 15 and 40° (normalization with respect to the cation peak).

remain essentially in the bulk of the solution. This conclusion is reached by considering both the relative intensity of the chloride peak with respect of solvent C 1s (showing no or only a small increase with respect to the relative intensity expected from a 0.5 *m* bulk solution) as well as the variation of the spectrum with respect to take-off angle. Thus, the angular variation between the Cl 2p peaks is found to be very similar to that found for the cation C 1s with respect to solvent C 1s. The nature of the surface active perchlorate complex may be inferred from the fact that the two negative ions do behave differently, hence specific chemical interactions have to be involved in the interaction with the cation. Moreover, we find that in comparison with corresponding counterion spectra (K 2p) obtained from fatty acid salts,[25] the enhancement observed for the perchlorate signal is high. These findings indicate that the perchlorate ions form a layer with direct contact to the cation overlayer without solvent separation.

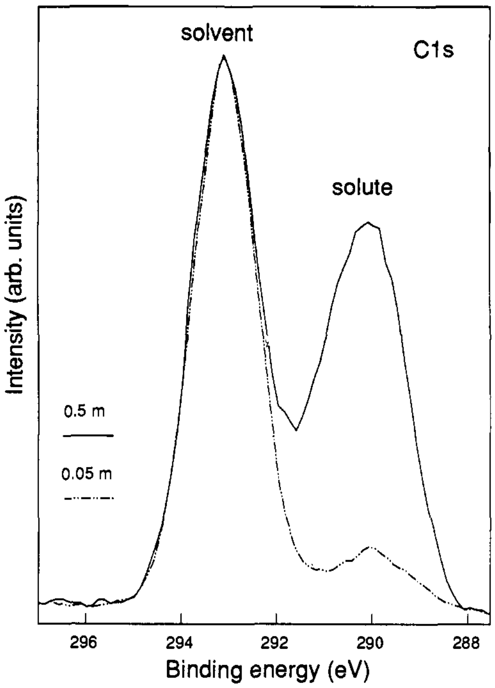

Figure 4. C 1s spectra obtained from 0.05 and 0.5 *m* solutions of $(IPrNBu_3)^+I^-$ in formamide at a take-off angle of 40° (normalization with respect to solvent C 1s).

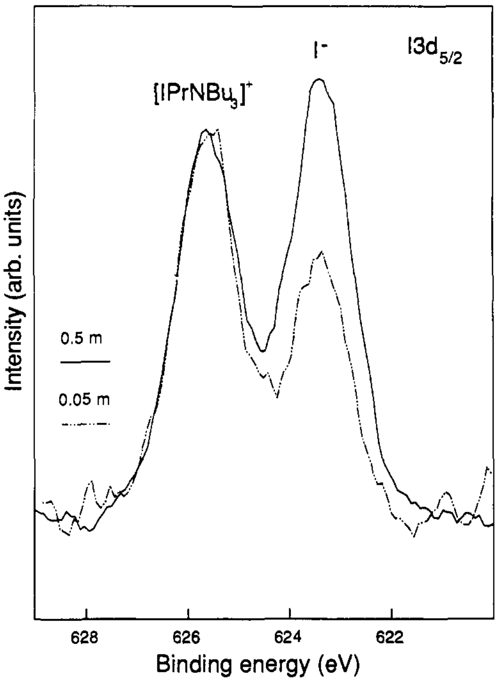

Figure 5. I $3d_{5/2}$ spectra obtained from 0.05 and 0.5 *m* solutions of $(IPrNBu_3)^+I^-$ in formamide at a take-off angle of 40° (normalization with respect to the cation peak).

In order to study in more detail the relation between cations and anions in these systems, we synthesized a salt, $(IPrNBu_3)I$, which contains iodine as a common element in both ions. In this way, the relative surface concentrations of cations and anions can be monitored with high accuracy due to the fact that these species give rise to two close-lying but well distinguishable I $3d_{5/2}$ photoelectron lines which can be simultaneously recorded. Iodine is advantageous also from the point of view that I 3d has a high photoelectric cross section. Figure 3 shows that I $3d_{5/2}$ spectrum from a 0.5 *m* solution of this compound at two different take-off angles. As can be seen there is a substantial binding energy shift between these two states. Also, the intensity ratio is very close to one,[26] which strongly indicates the presence in this case of direct ion pairing at the surface similar to the perchlorate case above. A small, but clearly measurable, angular variation in the ratio was detected. This can be interpreted in terms of a structure where the anions lie underneath the cations at the surface. The details of this structure are, however, difficult to assess from such a small variation. Therefore, a natural next step was to vary conditions in order to monitor possible changes in the spectrum. First, the concentration was decreased 10-fold to 0.05 *m*. As seen in the C 1s spectrum of Figure 4, this led to a substantial decrease in surface activity. The remaining intensity indicates that some activity persists, however. The estimated intensity enhancements of the solute C 1s peak were 2.8 and 4.5 at 0.5 and 0.05 *m*, respectively, with respect to solutions of non-surface-active salts of these concentrations. Possible hydrocarbon contamination of the surface (e.g. from pump oil) does not significantly affect the observed solute C 1s peak intensity (the solute cation C 1s/I 3d ratio at 0.05 *m* was found the same as at 0.5 *m*). Figure 5 shows the I $3d_{5/2}$ spectrum obtained at 0.05 *m* concentration (the spectrum is shown normalized to the cation peak of the spectrum obtained at 0.5 *m* concentration). As can be seen, the peak ratio in the I $3d_{5/2}$ spectrum has now significantly changed with a

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[26] The small deviation from one observed in the peak height ratio is due to a difference in width and probably also a difference in multielectron (valence electron shake-up and shake-off) excitations between the two iodine chemical states. Contamination of the sample (monitored by NMR to be ≤1%) is probably not the cause of the observed peak height ratio.

marked lowering of the anion peak. As mentioned above, the anion peak is not, however, reduced to the relative intensity expected from a homogeneous bulk solution. This would correspond to about 20% of the cation I $3d_{5/2}$ peak; instead we find a ratio close to 70%. As discussed further below, this change of the peak ratio with respect to that observed for the 0.5 *m* solution leads to further indications as to the structure of the surface region.

It is appropriate at this point to consider the structure expected on the basis of current theory of electric double layers of which the systems investigated here form a special case. The general model of the structure is that predicted by the Stern–Gouy–Chapman theory and further modified e.g. by Grahame (e.g. ref 27) involving closely bound inner and outer Helmholtz layer as well as the diffuse Gouy–Chapman layer. The Helmholtz layers are assumed to consist of specifically bound ions (inner) and ions which retain their solvation shells (outer) but reside at the surface plane. These latter ions are thus similar to, but conceptually distinguished from, the ions occurring in the diffuse layer. Whereas the Helmholtz layers are located within the first molecular layers of the solution, the diffuse layer extends 10–50 Å into the solution. Expressed differently (e.g. ref 28), the anions may be thought of as occurring in different ion pair situations which coexist at the surface: contact ion pairs (inner Helmholtz) and looser pairs separated by one molecule (solvent-shared; outer Helmholtz) or several molecules (solvent-separated; diffuse). In the "Helmholtz pairs" solvent molecular correlation would be expected to play a significant role, while in the "diffuse pairs" long-range electrostatic interactions are dominant. It should be mentioned that contact ion pairing in the solution bulk is not expected for monovalent ions in formamide due to the high dielectric constant.[5]

Returning to Figure 5 the lowering of the relative intensity of the anion peak may tentatively be interpreted in terms of the qualitative features of the double layer described above. Thus, it is natural to assume that the intensity lowering is to be associated with a dissolution of the closely bound parts, i.e. primarily the "inner Helmholtz" pairs. This can be understood in terms of the fact stated above, viz. the absence of bulk contact ion pairs. This shows that these pairs are normally unfavorable in this type of polar solvent and will appear only at the high concentrations existing at the surface. However, as long as surface activity persists the electrostatic interactions will sustain the looser pairs. The observed effect would be a combined consequence of dilution and lowering of the surface activity, leading to a substantial decrease in surface positive charge and hence electric field. It can be noted that the loss of surface activity upon dilution in this case is much more pronounced than for the fatty acid salts studied by us in a separate paper.[25] Our suggestion is thus from the comparison of data at 0.5 and 0.05 *m* that the topmost molecular layers seem to contain at least two types of ion pairs at the higher concentration.

Corroborative evidence for the above assertion may be obtained by mixing in other ions into the solution. When used as phase-transfer catalysts, the tetrabutylammonium salts with iodide and perchlorate show by far the highest transfer numbers between aqueous and organic phase.[29] This is in line with the formation of contact ion pairs at the interface in these cases, as clearly indicated by the present results (the difference between water and formamide is not believed to be crucial in such a qualitative comparison; neither is the difference between the organic phase and vacuum). It is thus of interest to study the effect of competition between these ions on the surface activity in these systems. Figure 6 shows the I $3d_{5/2}$ spectrum obtained from a solution of (IPrNBu$_3$)I (0.5 *m*) and KClO$_4$ (0.5 *m*) in formamide. As can be seen, the result in terms of relative intensities looks very similar to the spectrum obtained from the 0.05 *m* solution (cf. Figure 5). We thus interpret this spectrum on the same grounds, viz. as the replacement of the closely bound iodide ions by perchlorate ions. Such a replacement would primarily involve the contact ion pairs since these interactions are mainly of specific short-range nature. The iodide ions present at the surface in this solution mixture are mainly to be associated with looser ion pairing with the cation overlayer where the interactions are to a larger extent electrostatic. We reach this conclusion also on the basis of the measurement of the Cl 2p intensity enhancement; we find significant enhancement, but not as much as in the case Figure 2. From this

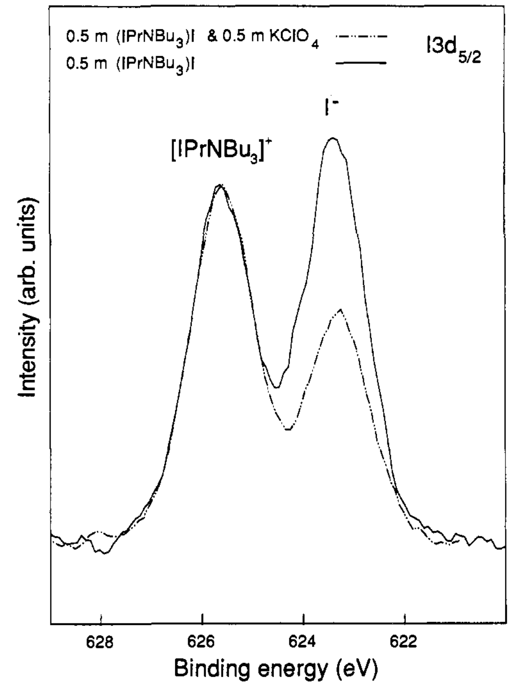

Figure 6. Comparison of I $3d_{5/2}$ spectra from two solutions of (IPrNBu$_3$)$^+$I$^-$ (0.5 *m*) in formamide at a take-off angle of 40° showing the effect of addition of KClO$_4$ (0.5 *m*) (normalization with respect to the cation peak).

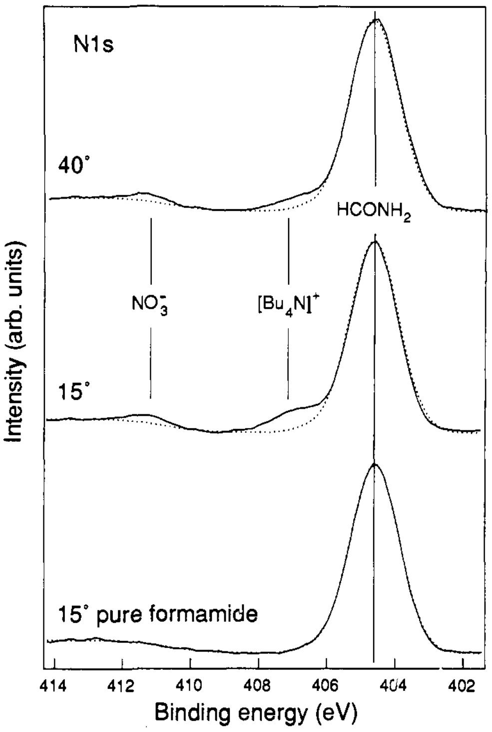

Figure 7. N 1s spectra of tetrabutylammonium nitrate (0.5 *m*) in formamide at take-off angles of 40 (top) and 15° (middle). The background shown in the spectra was obtained by fitting to the corresponding spectra of pure formamide (identical for 40 and 15°, bottom).

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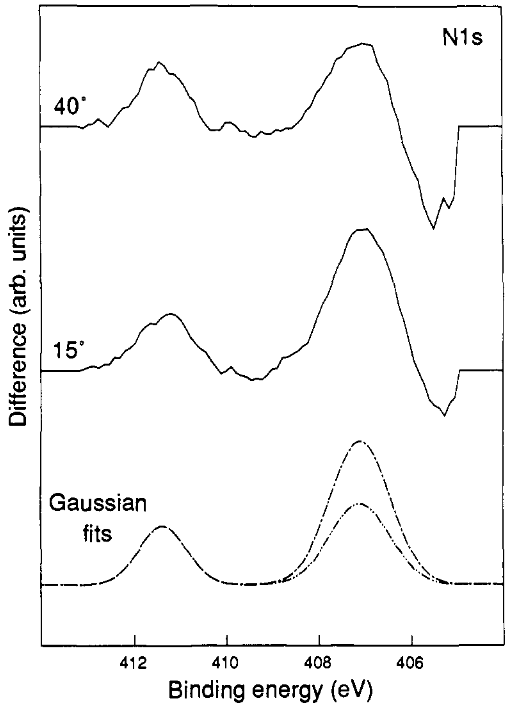

Figure 8. N 1s spectra obtained by subtraction of the pure formamide spectrum from the 40 and 15° spectra in Figure 7. The bottom shows Gaussian fits to the respective spectrum.

we assert that the perchlorate ions primarily occur in the topmost molecular layer of the solution. The above also agrees with the fact that the transfer number for perchlorate is somewhat higher than that for iodide.[29] Further investigations are under way on this and similar systems involving several concentrations as well as the influence of different cations.

As mentioned above larger differences are observed in the transfer numbers between aqueous and organic phase for different anions and one given phase-transfer cation.[29] Our results confirm the fact that iodide and perchlorate have the highest numbers, since these ions appear to more easily form closely bound layers at the surface. It is thus of interest to investigate anion cases having lower transfer numbers for a comparison of their surface structure to the iodide and perchlorate cases. The chloride ion is such a case; we have already shown in Figure 2 that this ion appears only weakly, if at all, segregated in the presence of perchlorate ions in the solution. Qualitatively, the tendency of an anion to segregate toward the surface will be a competition between the solvation forces and the ion pairing tendency at the surface. It is not obvious which of these factors will be dominant in a given case. We, and others,[16,19] have however noted a tendency for increased segregation in the halide series in going from chloride to iodide, in agreement with the relative transfer numbers. This has been explained in terms of the concept of solvent-enforced ion pairing.[30]

Another case showing a comparatively low transfer number is the nitrate ion.[29] Figure 7 shows the N 1s spectra obtained from a 0.5 m solution of $(Bu_4N)NO_3$ in formamide at two different take-off angles along with the spectrum of the same region obtained from pure formamide. The solute peaks in this case are small and lie moreover on a sloping background which requires the use of data of good statistical accuracy. Figure 7 yields solute peaks at 40° take-off angles which are enhanced by ~1.8 (NO_3^- peak at 411.5 eV) and ~2.5 (Bu_4N^+ peak at 407 eV) with respect to expected bulk intensities. The latter figure fits well with that obtained in the C 1s spectrum in comparing the cation and the solvent peaks. Changing the take-off angle to 15° shows clearly that the cation peak increases relative to the anion peak. Subtractions of the pure N 1s spectrum from the 40 and 15° spectra of the solution are displayed in Figure 8 to demonstrate the effect in more detail. This observed angular variation is significantly larger than that observed in the iodide case of Figure 3. We thus conclude that the nitrate compound does represent a different kind of surface activity, where the anions do not form close ion pairs with the cations at the surface but reside deeper into the bulk. The structure of the surface double layer is thus more diffuse in character which is indicative of the importance of bulk solvation forces in this case.

Conclusions

We have investigated solutions of a number of phase-transfer catalyst compounds with angular resolved electron spectroscopy. The results demonstrate the ability of the technique in directly probing the electric double layers formed at the solution–vacuum interface. The structure of the surface double layer has been found to be strongly dependent on the anion. The occurrence of closely bound anion layers in the cases of iodide and perchlorate is in agreement with high inter-phase-transfer numbers for these compounds. Conversely, a low number for nitrate is found to correlate with the absence of contact pairs at the surface and hence a more diffuse character of the anion layer. Further studies involving other ions (cations as well as anions), concentration dependencies, and different types of solvents are in progress. For example, it is to be expected that exchange of a protic solvent for an aprotic one will have significant effect on the tendency for formation of contact and solvent-shared ion pairs at the surface.

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